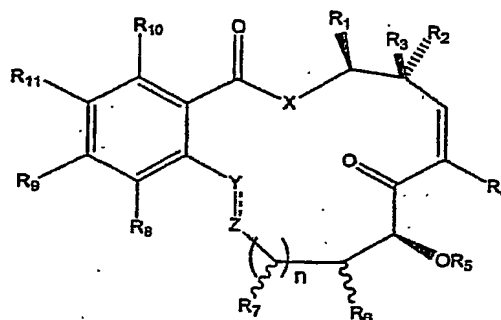


ART 34 AMDT
(all claim pages)

CLAIMS

We claim:

1. A compound having the structure:



(I)

or pharmaceutically acceptable salt, ester, or salt of ester thereof;

wherein R_1 is hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl moiety; or

R_1 and R_2 , when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms; or

R_1 and R_3 , when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms;

R_4 is hydrogen or halogen;

R_5 is hydrogen, an oxygen protecting group or a prodrug;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or an aliphatic moiety optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

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wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$, $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an aliphatic moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;


R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $C=O$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $C=O$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or aliphatic, or R_{17} and R_{18} taken together is $-O-$, $-CH_2-$ or $-NR_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond;

with the proviso that when n is 1; X is O; R_1 is methyl; R_2 , R_3 , R_7 and R_{11} are each hydrogen; R_5 is hydrogen, C_{1-4} alkyl or $-C(=O)C_{1-4}$ alkyl; R_6 is hydrogen, OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; and R_9 is OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; then one or more if the following groups do not occur simultaneously as defined:

- (i) R_4 is hydrogen; R_{10} and R_8 are independently OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; and Y-Z is $-CH_2CH_2-$ or $-CH=CH-$;
- (ii) R_4 and R_8 are each hydrogen; R_{10} is OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; and Y-Z is $-CHR^YCHR^Z-$, $-CH=CH-$ or ; wherein R^Y and R^Z are independently hydrogen, C_{1-4} alkyl or C_{1-4} alkanoyl; and
- (iii) R_4 and R_{10} are each hydrogen, OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; R_8 is hydrogen, OH, halogen, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; and Y-Z is $-CH_2CH_2-$, $-CH=CH-$ or $-C(=O)CH_2-$.

2. The compound of claim 1, where the following groups do not occur simultaneously as defined:

- X is oxygen,
- R_1 is methyl,
- R_2 and R_3 are each hydrogen,
- R_4 is hydrogen,
- R_5 is hydrogen, C_{1-6} alkyl or C_{1-6} alkanoyl,
- R_6 is OR' , where R' is hydrogen, C_{1-6} alkyl or C_{1-6} alkanoyl with S-configuration,
- R_7 is hydrogen,
- Y and Z together represent $-CHR_{17}-CHR_{18}-$ or $-CR_{17}=CR_{18}-$, wherein R_{17} and R_{18} are independently hydrogen, or when Y and Z are $-CHR_{17}-CHR_{18}$, R_{17} and R_{18} taken together are $-O-$;
- R_8 is hydrogen or OR' , where R' is hydrogen, C_{1-6} alkyl or C_{1-6} alkanoyl,
- R_9 is OR' , where R' is hydrogen, C_{1-6} alkyl or C_{1-6} alkanoyl,
- R_{10} is OR'' , where R'' is hydrogen, C_{1-6} alkyl or C_{1-6} alkanoyl; and
- R^{11} is hydrogen.

3. The compound of claim 1, wherein:

- R_1 is hydrogen, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl, wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R_1 and R_3 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R_4 is hydrogen or halogen;

R_5 is hydrogen or a protecting group;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, C_{1-6} alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

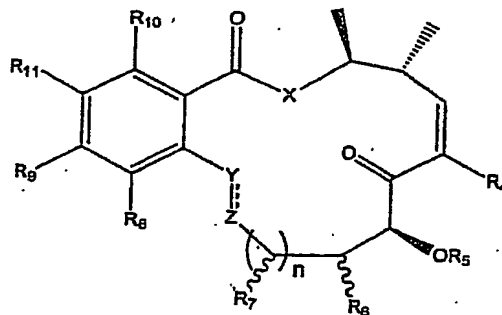
R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $C=O$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $C=O$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or C_{1-6} alkyl, or R_{17} and R_{18} taken together is $-O-$, $-CH_2-$ or $-NR_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond.

4. The compound of claim 3, where X is oxygen and n is 1.
5. The compound of claim 3, where R_4 is halogen.
6. The compound of claim 3, where R_4 is fluorine.
7. The compound of claim 3, where Y and Z together represent $-CH=CH-$.
8. The compound of claim 3, where Y and Z together represent trans $-CH=CH-$.

9. The compound of claim 3, wherein R_1 and R_2 are each methyl and R_3 is hydrogen and the compound has the structure:



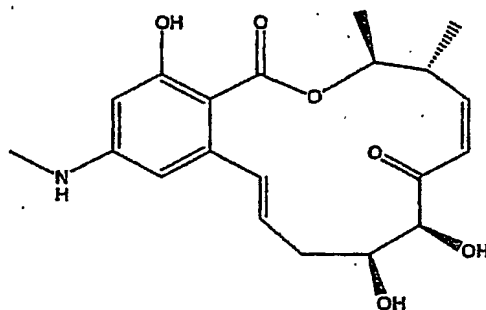
wherein R_4 - R_{11} , n , X , Y and Z are as defined in claim 3.

10. The compound of claim 9, wherein X is oxygen and n is 1.
11. The compound of claim 9, wherein R_4 is halogen.

20. The compound of claim 15, wherein X is oxygen, n is 1, R₁ and R₂ are each methyl, R₃ is hydrogen, R₄ is halogen, and Y and Z together represent -CH=CH-.

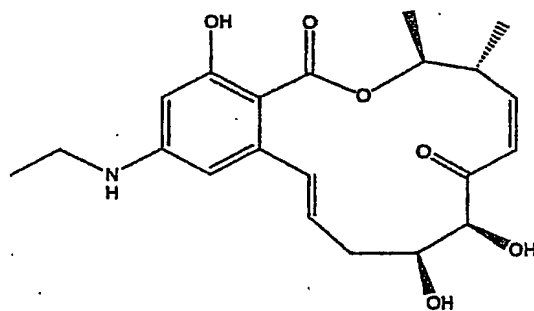
21. The compound of claim 18 or 20, wherein -CH=CH- is trans.

22. A compound having the structure:



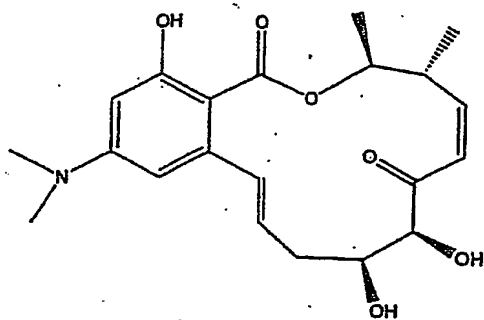
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

23. A compound having the structure:



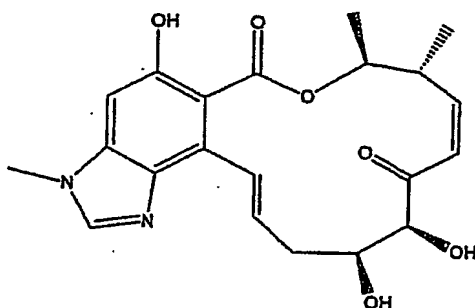
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

24. A compound having the structure:



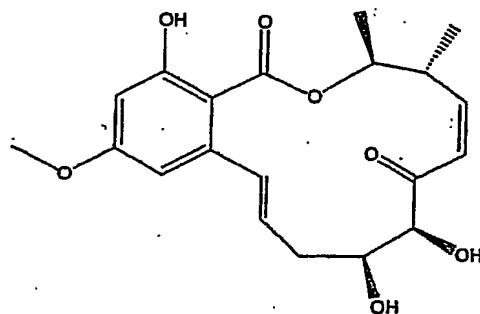
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

25. A compound having the structure:



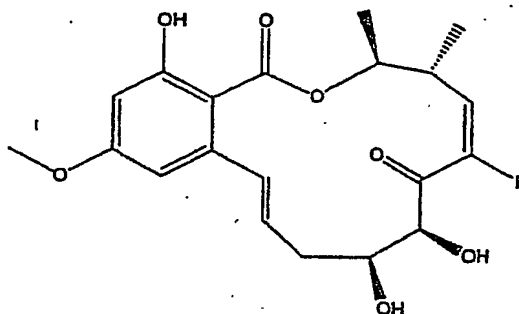
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

26. A compound having the structure:



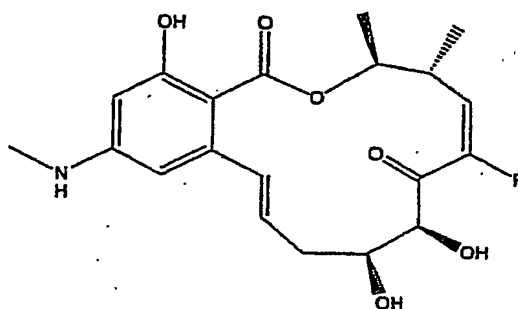
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

27. A compound having the structure:



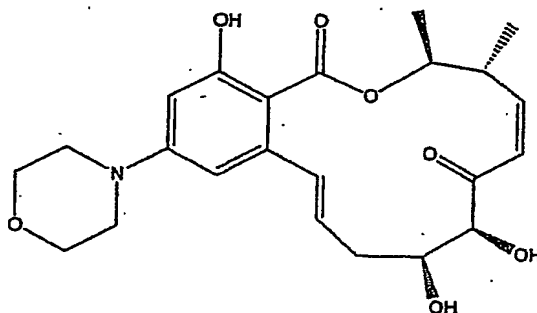
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

28. A compound having the structure:



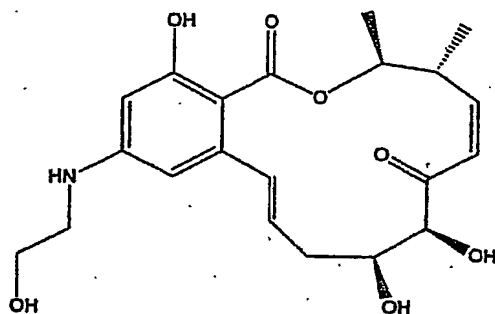
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

29. A compound having the structure:



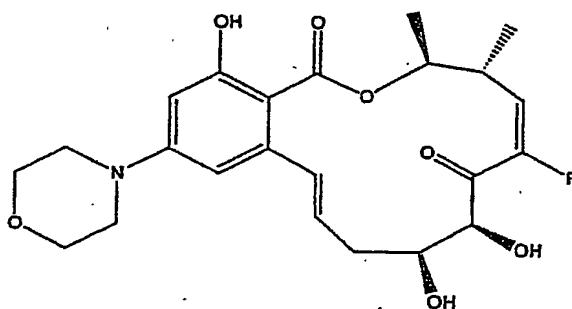
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

30. A compound having the structure:



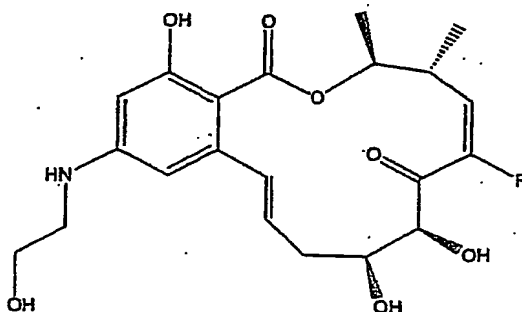
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

31. A compound having the structure:



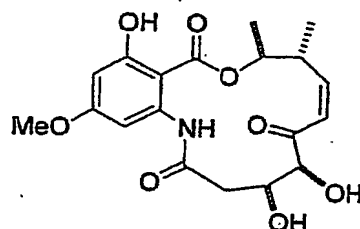
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

32. A compound having the structure:



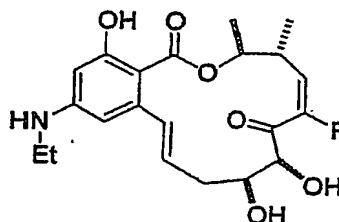
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

33. A compound having the structure:



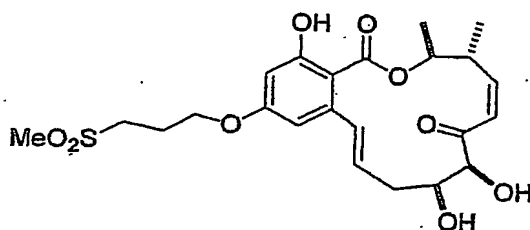
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

34. A compound having the structure:



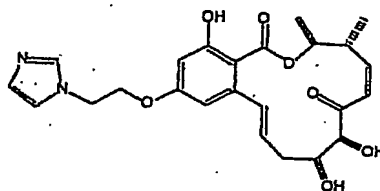
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

35. A compound having the structure:



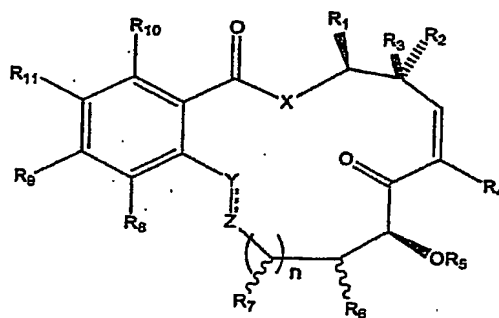
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

36. A compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof.

37. A pharmaceutical composition comprising:
a compound having the structure:



(I)

or pharmaceutically acceptable salt, ester, or salt of ester thereof;

wherein R_1 is hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl moiety; or

R_1 and R_2 , when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms; or

R_1 and R_3 , when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms;

R_4 is hydrogen or halogen;

R_5 is hydrogen, an oxygen protecting group or a prodrug;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or an aliphatic moiety optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or $-N(\text{alkyl})$, or wherein X_2-R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$, $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an aliphatic moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;


R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $\text{C}=\text{O}$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $\text{C}=\text{O}$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or aliphatic, or R_{17} and R_{18} taken together is $-\text{O}-$, $-\text{CH}_2-$ or $-\text{NR}_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond; and

a pharmaceutically acceptable carrier;

with the proviso that when n is 1; X is O; R_1 is methyl; R_2 , R_3 , R_7 and R_{11} are each hydrogen; R_5 is hydrogen, C_{1-4} alkyl or $-\text{C}(=\text{O})\text{C}_{1-4}$ alkyl; R_6 is hydrogen, OH, C_{1-4} alkoxy or $-\text{OC}(=\text{O})\text{C}_{1-4}$ alkyl; and R_9 is OH, C_{1-4} alkoxy or $-\text{OC}(=\text{O})\text{C}_{1-4}$ alkyl; then one or more if the following groups do not occur simultaneously as defined:

- (i) R_4 is hydrogen; R_{10} and R_8 are independently OH, C_{1-4} alkoxy or $-\text{OC}(=\text{O})\text{C}_{1-4}$ alkyl; and Y-Z is $-\text{CH}_2\text{CH}_2-$ or $-\text{CH}=\text{CH}-$;
- (ii) R_4 and R_8 are each hydrogen; R_{10} is OH, C_{1-4} alkoxy or $-\text{OC}(=\text{O})\text{C}_{1-4}$ alkyl; and Y-Z is $-\text{CHR}^Y\text{CHR}^Z-$, $-\text{CH}=\text{CH}-$ or ; wherein R^Y and R^Z are independently hydrogen, C_{1-4} alkyl or C_{1-4} alkanoyl; and

- (iii) R_4 and R_{10} are each hydrogen, OH, C_{1-4} alkoxy or $-\text{OC}(=\text{O})\text{C}_{1-4}$ alkyl; R_8 is hydrogen, OH, halogen, C_{1-4} alkoxy or $-\text{OC}(=\text{O})\text{C}_{1-4}$ alkyl; and Y-Z is $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$ or $-\text{C}(=\text{O})\text{CH}_2-$.

38. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit NF- κ B activation.

39. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit AP-1 activation.

40. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit a protein kinase.

41. The pharmaceutical composition of claim 39, wherein the protein kinase is MEKK1, MEK1, VEGFr or PDGFr.

42. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to inhibit proliferation of cancerous cells and angiogenesis on solid tumors.

43. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to have an anti-inflammatory effect.

44. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to treat psoriasis.

45. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to reduce skin photodamage.

46. The pharmaceutical composition of claim 37, wherein the compound is present in an amount effective to prevent restenosis.

47. The pharmaceutical composition of claim 37, where:

R_1 is hydrogen, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R_1 and R_3 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R_4 is hydrogen or halogen;

R_5 is hydrogen or a protecting group;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, C_{1-6} alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or $-N(\text{alkyl})$, or wherein X_2-R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$, $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $C=O$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $C=O$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or C_{1-6} alkyl, or R_{17} and R_{18} taken together is $-O-$, $-CH_2-$ or $-NR_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond.

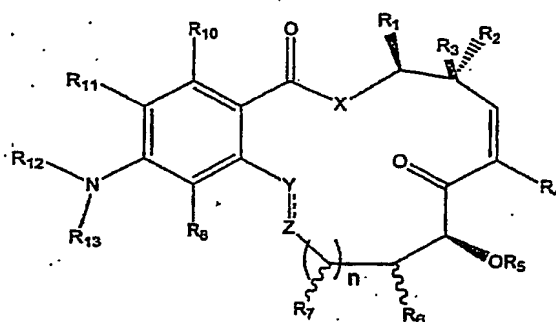
48. The pharmaceutical composition of claim 47, where X is oxygen and n is 1.

49. The pharmaceutical composition of claim 47, where R_4 is halogen.

50. The pharmaceutical composition of claim 49, where R_4 is fluorine.

51. The pharmaceutical composition of claim 47, where Y and Z together represent $-CH=CH-$.

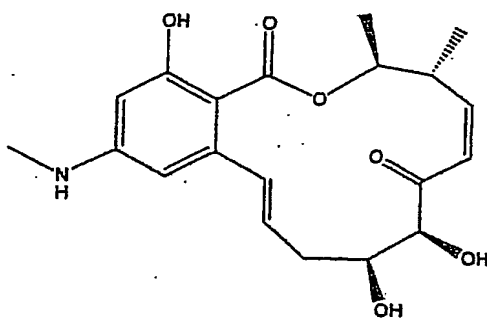
52. The pharmaceutical composition of claim 51, wherein $-CH=CH-$ is trans.



R₁₃ and R₈ may, when taken together, form a cyclic ring containing 1 to 4

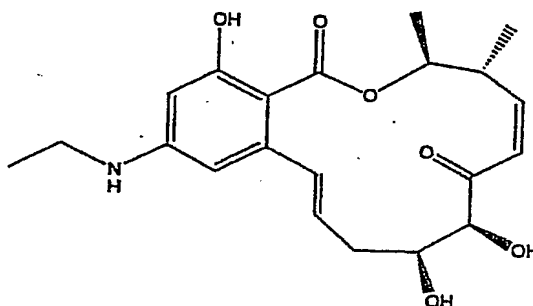
carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydrogen, alkyloxy, amino, alkylamino, aminoalkyl, and halogen.

60. The pharmaceutical composition of claim 59, wherein X is oxygen and n is 1.
61. The pharmaceutical composition of claim 59, wherein R₄ is halogen.
62. The pharmaceutical composition of claim 59, wherein Y and Z together represent -CH=CH-.
63. The pharmaceutical composition of claim 59, wherein R₁ and R₂ are each methyl and R₃ is hydrogen.
64. The pharmaceutical composition of claim 59 wherein X is oxygen, n is 1, R₁ and R₂ are each methyl, R₃ is hydrogen, R₄ is halogen, and Y and Z together represent -CH=CH-.
65. The pharmaceutical composition of claim 63 or 64 wherein -CH=CH- is trans.
66. A pharmaceutical composition comprising:
a compound having the structure:



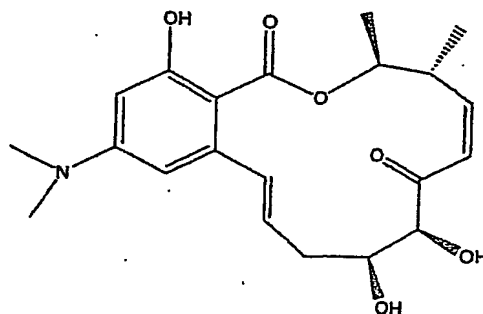
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

67. A pharmaceutical composition comprising:
a compound having the structure:



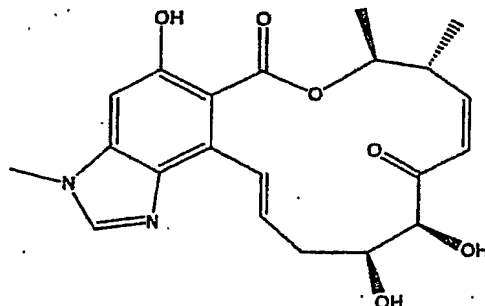
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

68. A pharmaceutical composition comprising:
a compound having the structure:



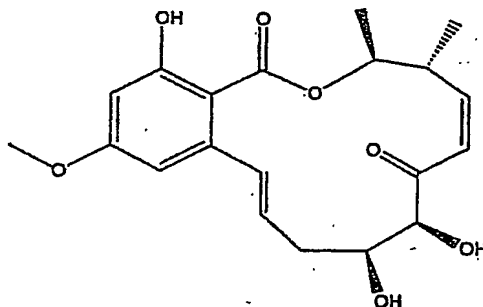
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

69. A pharmaceutical composition comprising:
a compound having the structure:



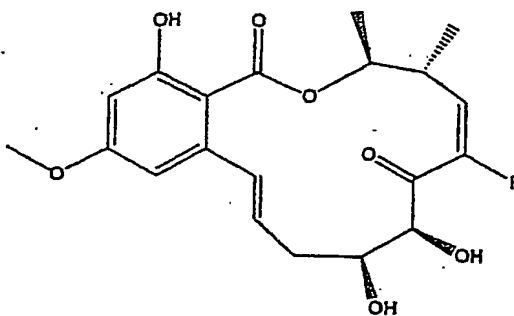
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

70. A pharmaceutical composition comprising:
a compound having the structure:



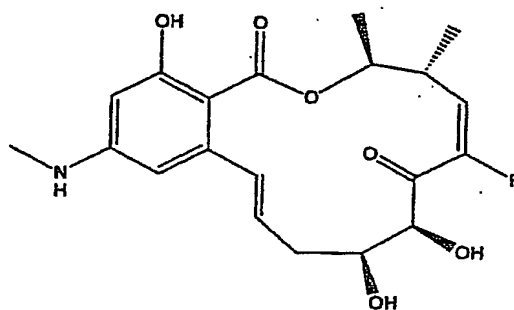
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

71. A pharmaceutical composition comprising:
a compound having the structure:



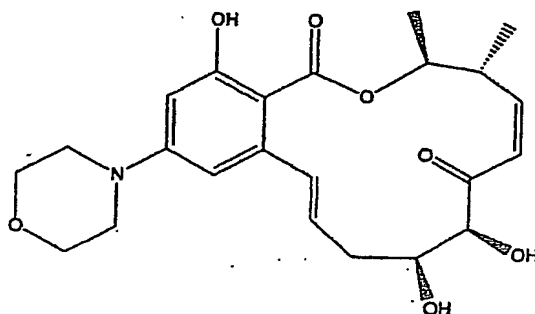
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

72. A pharmaceutical composition comprising:
a compound having the structure:



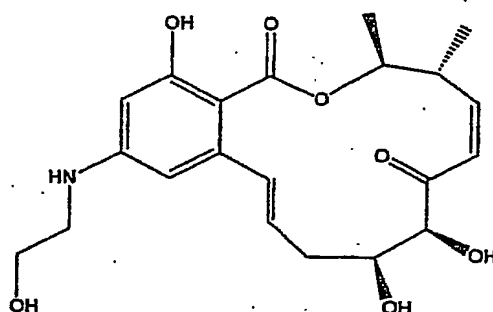
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

73. A pharmaceutical composition comprising:
a compound having the structure:



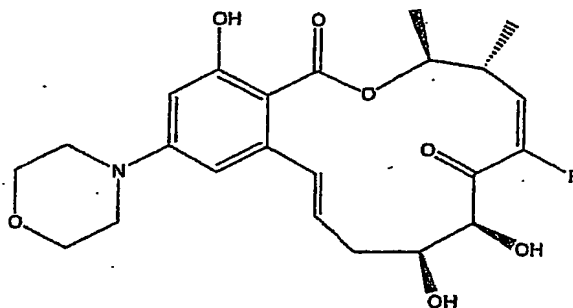
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

74. A pharmaceutical composition comprising:
a compound having the structure:



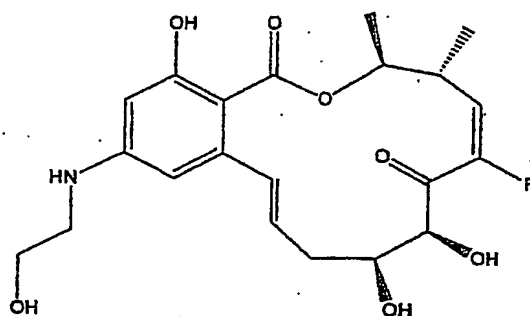
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

75. A pharmaceutical composition comprising:
a compound having the structure:



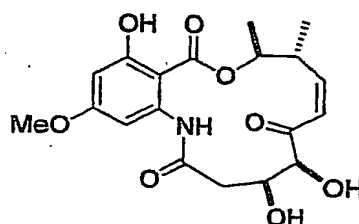
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

76. A pharmaceutical composition comprising:
a compound having the structure:



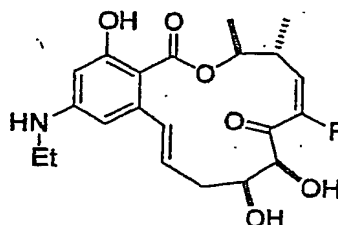
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

77. A pharmaceutical composition comprising:
a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

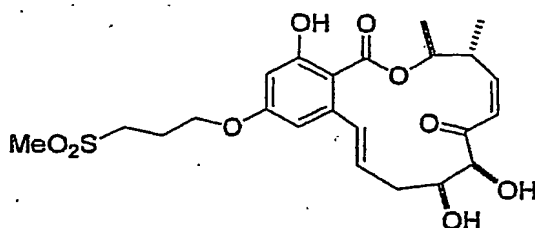
78. A pharmaceutical composition comprising:
a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

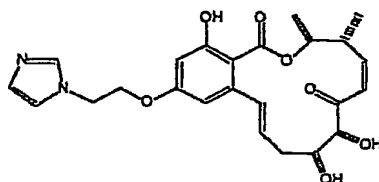
79. A pharmaceutical composition comprising:

a compound having the structure:



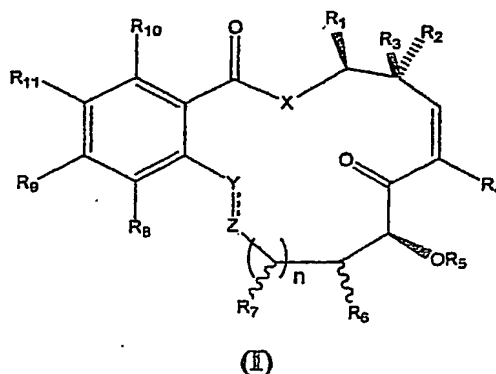
or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

80. A pharmaceutical composition comprising:
a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof; and
a pharmaceutically acceptable carrier.

81. A topical pharmaceutical composition for preventing or treating UVB-induced
photodamage comprising:
a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof;

wherein R_1 is hydrogen, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R_1 and R_3 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R_4 is hydrogen or halogen;

R_5 is hydrogen or a protecting group;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, C_{1-6} alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences

of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $C=O$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $C=O$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or C_{1-6} alkyl, or R_{17} and R_{18} taken together is $-O-$, $-CH_2-$ or $-NR_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond; and

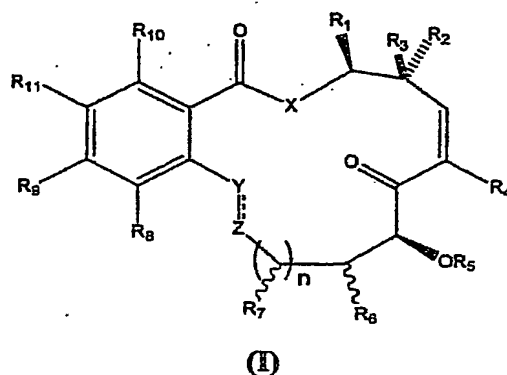
a pharmaceutically acceptable carrier;

wherein the compound is present in an amount effective to prevent or treat UVB-induced photodamage.

82. The pharmaceutical composition of claim 81, further comprising a cosmetic ingredient.

83. The pharmaceutical composition of claim 82, wherein the cosmetic ingredient is a sunscreen.

84. A method for treating an inflammatory and/or autoimmune disorder or a disorder resulting from increased angiogenesis and/or cell proliferation comprising:
administering to a subject in need thereof a therapeutically effective amount of a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof;

wherein R_1 is hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl moiety; or

R_1 and R_2 , when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms; or

R_1 and R_3 , when taken together, may form a substituted or unsubstituted, saturated or unsaturated cyclic ring of 3 to 8 carbon atoms;

R_4 is hydrogen or halogen;

R_5 is hydrogen, an oxygen protecting group or a prodrug;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or an aliphatic moiety optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH , or $-N(alkyl)$, or wherein X_2-R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$, $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an aliphatic moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R_{11} is hydrogen, hydroxyl or protected hydroxyl;


X is absent or is O , NH , N -alkyl, CH_2 or S ;

Y is CHR_{17} , O , $C=O$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O , $C=O$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or aliphatic; or R_{17} and R_{18} taken together is $-O-$, $-CH_2-$ or $-NR_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond; and

a pharmaceutically acceptable carrier or diluent;

with the proviso that when n is 1; X is O; R_1 is methyl; R_2, R_3, R_7 and R_{11} are each hydrogen; R_5 is hydrogen, C_{1-4} alkyl or $-C(=O)C_{1-4}$ alkyl; R_6 is hydrogen, OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; and R_9 is OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; then one or more if the following groups do not occur simultaneously as defined:

- (i) R_4 is hydrogen; R_{10} and R_8 are independently OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; and $Y-Z$ is $-CH_2CH_2-$ or $-CH=CH-$; and
- (ii) R_4 and R_8 are each hydrogen; R_{10} is OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$

$_4$ alkyl; and $Y-Z$ is $-CHR^YCHR^Z-$, $-CH=CH-$ or ; wherein R^Y and R^Z are independently hydrogen, C_{1-4} alkyl or C_{1-4} alkanoyl; and

- (iii) R_4 and R_{10} are each hydrogen, OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; R_8 is hydrogen, OH, halogen, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; and $Y-Z$ is $-CH_2CH_2-$, $-CH=CH-$ or $-C(=O)CH_2-$; whereby the compound induces mRNA degradation and the method is for treating a disorder resulting from cell proliferation.

85. The method of claim 84, wherein the method is for treating a disorder selected from the group consisting of rheumatoid arthritis, psoriasis, asthma, cancer, sepsis, inflammatory bowel disease, atopic dermatitis, Crohn's disease, and autoimmune disorders.

86. The method of claim 84, wherein the method is for treating rheumatoid arthritis.

87. The method of claim 84, wherein the method is for treating psoriasis.

88. The method of claim 84, wherein the method is for treating asthma.

89. The method of claim 84, wherein:

R_1 is hydrogen, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R_1 and R_3 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R_4 is hydrogen or halogen;

R_5 is hydrogen or a protecting group;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, C_{1-6} alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or -N(alkyl), or wherein X_2 - R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R_{11} is hydrogen, hydroxyl or protected hydroxyl;

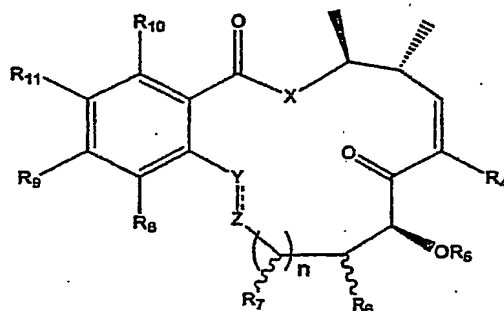
X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $C=O$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $C=O$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or C_{1-6} alkyl, or R_{17} and R_{18} taken together is $-O-$, $-CH_2-$ or $-NR_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond.

90. The method of claim 89, wherein in the compound X is oxygen and n is 1.
91. The method of claim 89, wherein in the compound R_4 is halogen.
92. The method of claim 89 is wherein in the compound R_4 is fluorine.
93. The method of claim 89, wherein in the compound Y and Z together represent $CH=CH-$

94. The method of claim 93, wherein in the compound Y and Z together represent $\text{trans}-\text{CH}=\text{CH}-$.

95. The method of claim 89, comprising administering a compound wherein R_1 and R_2 are each methyl and R_3 is hydrogen and the compound has the structure:



wherein $\text{R}_4\text{-R}_{11}$, n , X , Y and Z are as defined in claim 88.

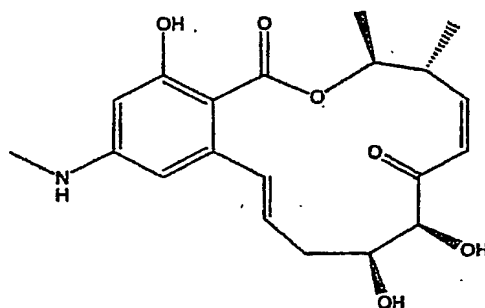
96. The method of claim 95, wherein in the compound X is oxygen and n is 1.

97. The method of claim 95, wherein in the compound R_4 is halogen.

106. The method of claim 101, wherein in the compound X is oxygen, n is 1, R₁ and R₂ are each methyl, R₃ is hydrogen, R₄ is halogen, and Y and Z together represent -CH=CH-.

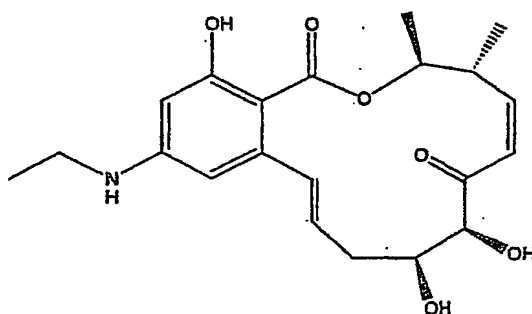
107. The method of claim 105 or 106, wherein in the compound -CH=CH- is trans.

108. The method of claim 84, comprising administering a compound having the structure:



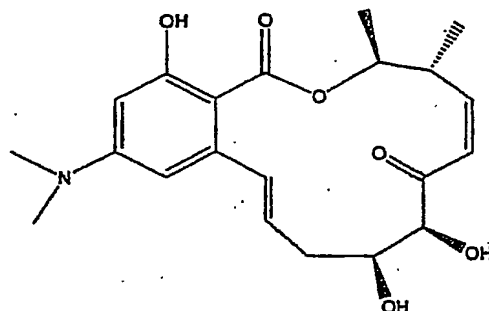
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

109. The method of claim 84, comprising administering a compound having the structure:



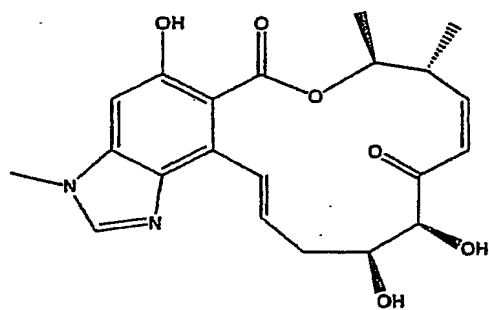
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

110. The method of claim 84, comprising administering a compound having the structure:



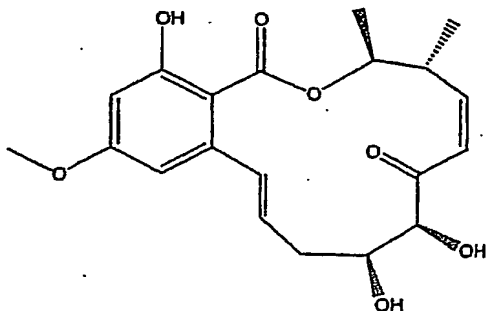
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

111. The method of claim 84, comprising administering a compound having the structure:



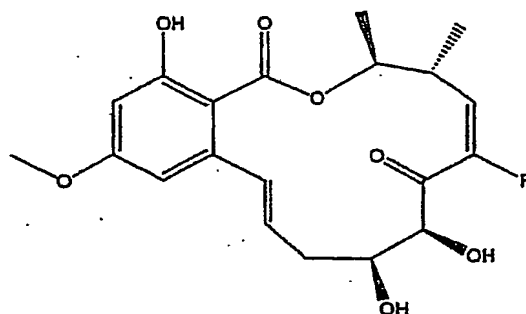
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

112. The method of claim 84, comprising administering a compound having the structure:



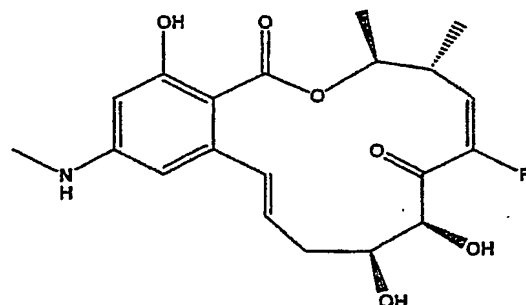
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

113. The method of claim 84, comprising administering a compound having the structure:



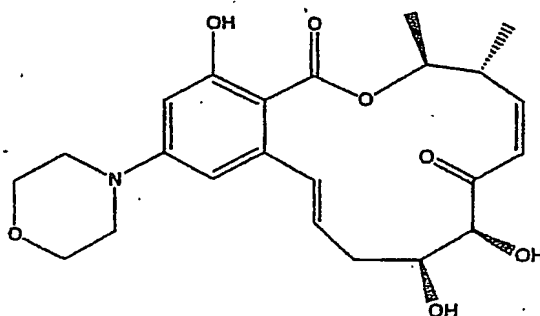
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

114. The method of claim 84, comprising administering a compound having the structure:



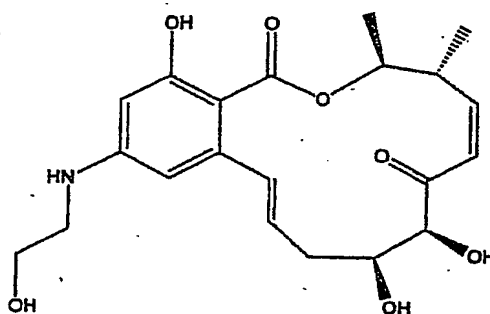
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

115. The method of claim 84, comprising administering a compound having the structure:



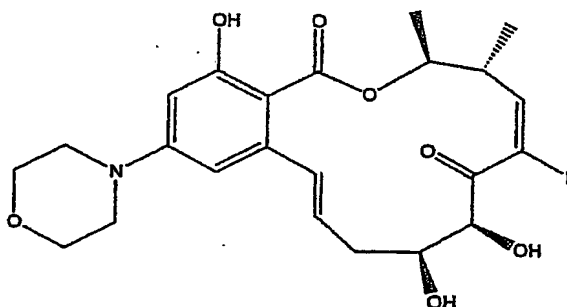
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

116. The method of claim 84, comprising administering a compound having the structure:



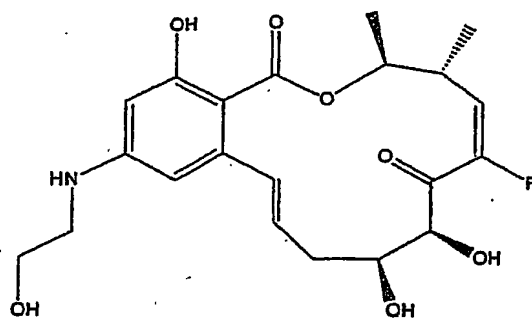
or pharmaceutically acceptable salt, ester, or salt of ester thereof.

117. The method of claim 84, comprising administering a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof.

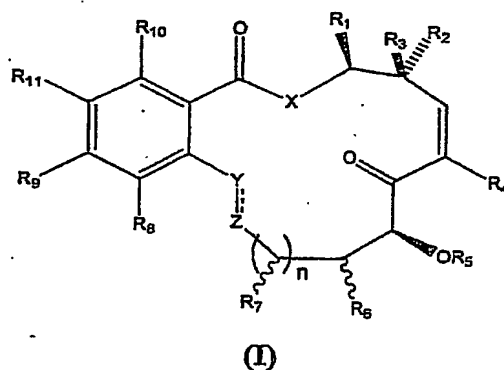
118. The method of claim 84, comprising administering a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof.

119. A method for providing protection against UVB-induced photodamage to a subject, said method comprising:

Administering to the subject in need thereof a composition comprising a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof;

wherein R_1 is hydrogen, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R_1 and R_3 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R_4 is hydrogen or halogen;

R_5 is hydrogen or a protecting group;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, C_{1-6} alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or $-N(\text{alkyl})$, or wherein X_2-R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each

occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-\text{SO}_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $\text{C}=\text{O}$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $\text{C}=\text{O}$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or C_{1-6} alkyl, or R_{17} and R_{18} taken together is $-\text{O}-$, $-\text{CH}_2-$ or $-\text{NR}_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond; and

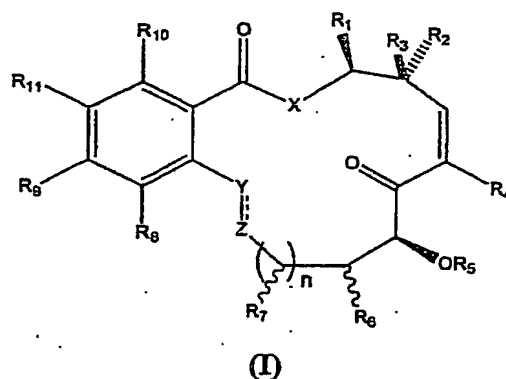
a pharmaceutically acceptable carrier or diluent.

120. The method of claim 119, wherein in the step of administering, the composition is administered topically.

121. The method of claim 119, wherein the photodamage is skin wrinkles.

122. The method of claim 119, wherein the photodamage is a skin cancer.

123. A method for preventing or reducing the rate of restenosis, comprising:
inserting a stent into an obstructed blood vessel, the stent having a generally tubular structure, the surface of the structure being coated with (or otherwise adapted to release) a composition comprising a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof;

wherein R_1 is hydrogen, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R_1 and R_3 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R_4 is hydrogen or halogen;

R_5 is hydrogen or a protecting group;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

n is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, C_{1-6} alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or $-N(\text{alkyl})$, or wherein X_2-R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$, $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-SO_2(R_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;


R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

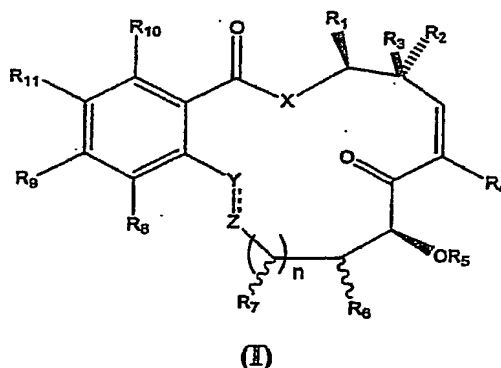
Y is CHR_{17} , O, $C=O$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $C=O$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or C_{1-6} alkyl, or R_{17} and R_{18} taken together is $-O-$, $-CH_2-$ or $-NR_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond; and optionally a pharmaceutically acceptable carrier or diluent;

such that the obstruction is eliminated and the composition is delivered in amounts effective to prevent or reduce the rate of restenosis;

with the proviso that the following groups do not occur simultaneously as defined: n is 1; X is O; R_1 is methyl; R_2, R_3, R_4, R_7, R_8 and R_{11} are each hydrogen; R_5 is hydrogen, C_{1-4} alkyl or $-C(=O)C_{1-4}$ alkyl; R_6 is hydrogen, OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl; R_9 and R_{10} are independently OH, C_{1-4} alkoxy or $-OC(=O)C_{1-4}$ alkyl;

and $Y-Z$ is $-CHR^YCHR^Z-$, $-CH=CH-$ or ; wherein R^Y and R^Z are independently hydrogen, C_{1-4} alkyl or C_{1-4} alkanoyl.

124. A method for expanding the lumen of a body passageway, comprising:
inserting a stent into the passageway, the stent having a generally tubular structure, the surface of the structure being coated with (or otherwise adapted to release) a composition comprising a compound having the structure:



or pharmaceutically acceptable salt, ester, or salt of ester thereof;

wherein R_1 is hydrogen, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl;

R_2 and R_3 are each independently hydrogen, halogen, hydroxyl, protected hydroxyl, straight or branched C_{1-6} alkyl, straight or branched C_{1-6} heteroalkyl, or aryl,

wherein the alkyl, heteroalkyl, and aryl groups may optionally be substituted with one or more occurrences of halogen, hydroxyl or protected hydroxyl; or

R_1 and R_2 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen; or

R_1 and R_3 , when taken together, may form a saturated or unsaturated cyclic ring of 3 to 8 carbon atoms, optionally substituted with one or more occurrences of halogen;

R_4 is hydrogen or halogen;

R_5 is hydrogen or a protecting group;

R_6 is hydrogen, hydroxyl, or protected hydroxyl;

m is 0-2;

R_7 , for each occurrence, is independently hydrogen, hydroxyl, or protected hydroxyl;

R_8 is hydrogen, halogen, hydroxyl, protected hydroxyl, alkyloxy, or C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, SR_{12} , or $NR_{12}R_{13}$;

R_9 is hydrogen, halogen, hydroxyl, protected hydroxyl, OR_{12} , SR_{12} , $NR_{12}R_{13}$, $-X_1(CH_2)_pX_2-R_{14}$, or is C_{1-6} alkyl optionally substituted with hydroxyl, protected hydroxyl, halogen, amino, protected amino, or $-X_1(CH_2)_pX_2-R_{14}$;

wherein R_{12} and R_{13} are, independently for each occurrence, hydrogen, C_{1-6} alkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or a protecting group, or R_{12} and R_{13} , taken together may form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms, and each of R_{12} and R_{13} are optionally further substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen,

wherein X_1 and X_2 are each independently absent, or are oxygen, NH, or $-N(\text{alkyl})$, or wherein X_2-R_{14} together are N_3 or are a saturated or unsaturated heterocyclic moiety,

p is 2-10, and

R_{14} is hydrogen, or an aryl, heteroaryl, alkylaryl, or alkylheteroaryl moiety, or is $-(C=O)NHR_{15}$ $-(C=O)OR_{15}$, or $-(C=O)R_{15}$, wherein each

occurrence of R_{15} is independently hydrogen, alkyl, heteroalkyl, aryl, heteroaryl, alkylaryl, or alkylheteroaryl, or R_{14} is $-\text{SO}_2(\text{R}_{16})$, wherein R_{16} is an alkyl moiety, wherein one or more of R_{14} , R_{15} , or R_{16} are optionally substituted with one or more occurrences of hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen; or

R_8 and R_9 may, when taken together, form a saturated or unsaturated cyclic ring containing 1 to 4 carbon atoms and 1 to 3 nitrogen or oxygen atoms and is optionally substituted with hydroxyl, protected hydroxyl, alkyloxy, amino, protected amino, alkylamino, aminoalkyl, or halogen;

R_{10} is hydrogen, hydroxyl, protected hydroxyl, amino, or protected amino;

R_{11} is hydrogen, hydroxyl or protected hydroxyl;

X is absent or is O, NH, N-alkyl, CH_2 or S;

Y is CHR_{17} , O, $\text{C}=\text{O}$, CR_{17} or NR_{17} ; and Z is CHR_{18} , O, $\text{C}=\text{O}$, CR_{18} or NR_{18} , wherein each occurrence of R_{17} and R_{18} is independently hydrogen or C_{1-6} alkyl, or R_{17} and R_{18} taken together is $-\text{O}-$, $-\text{CH}_2-$ or $-\text{NR}_{19}-$, wherein R_{19} is hydrogen or C_{1-6} alkyl, and Y and Z may be connected by a single or double bond; and optionally

a pharmaceutically acceptable carrier or diluent;

such that the passageway is expanded.

125. The method of claim 124, wherein the lumen of a body passageway is expanded in order to eliminate a biliary, gastrointestinal, esophageal, tracheal/bronchial, urethral and/or vascular obstruction.

126. The method of claim 125, wherein the lumen of a body passageway is expanded in order to eliminate a vascular obstruction.

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